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DIFLUORAMINO ENERGETIC MATERIALS

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Report Documentation Page

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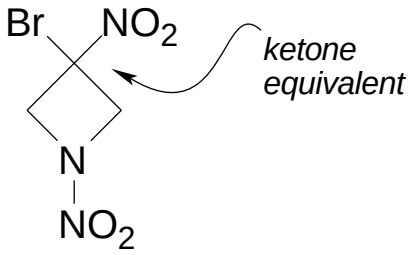
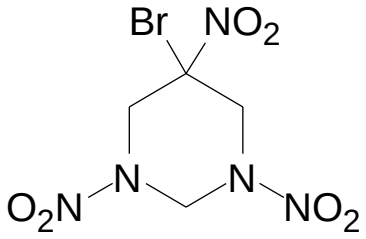
Difluoramino Nitramines

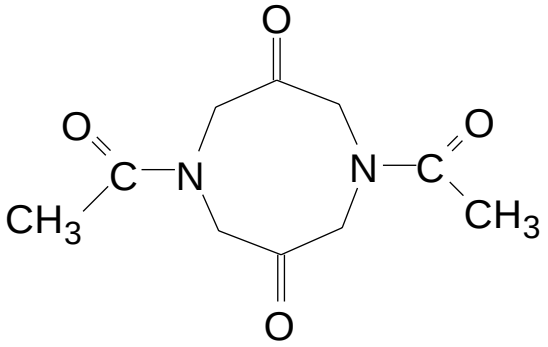
- The concept: Archibald & Baum (Fluorochem, 1988)
- NF_2 derivatives $\rightarrow$ higher energy $\rightarrow$ improved performance
- Mix of NF_2 and NO_2 to maintain insensitivity

Community Meeting (China Lake, 1989)

- Latest property predictions presented
- Intermediates toward target compounds first presented

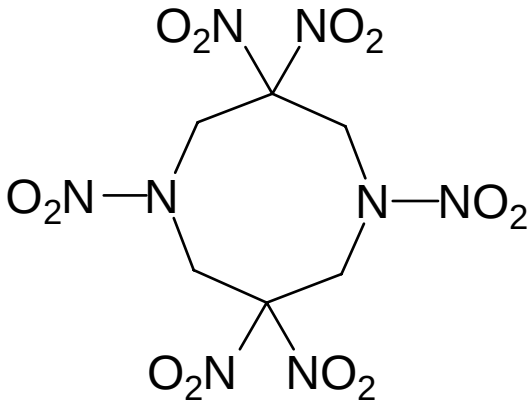




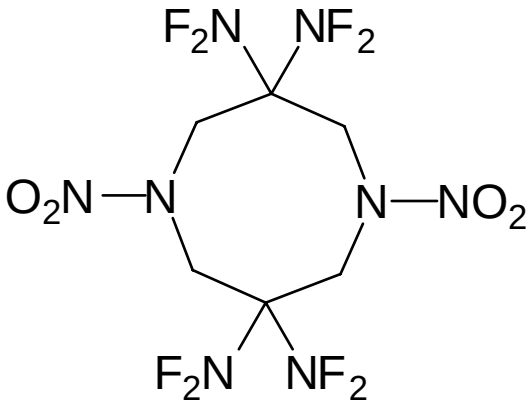


(Chapman, Fluorochem)

Tetrakis(difluoramino)octahydro-1,5-**d**initro-1,5-**d**ia**z**ocine (**TEDDZ**)

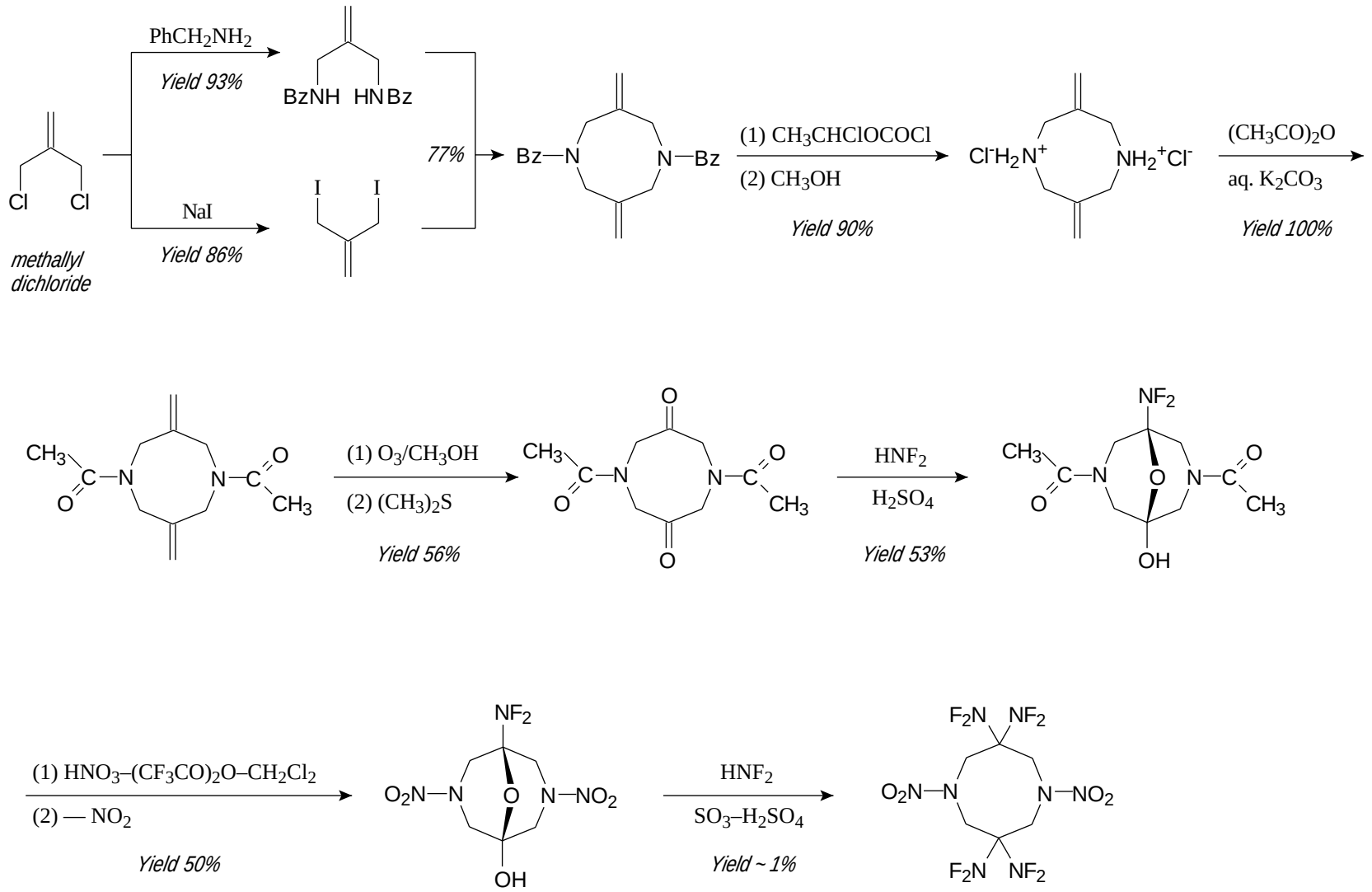


"HNDZ"
T.B. Brill *et al.*
J. Phys. Chem.
1985, *89*, 4317



"TEDDZ"
or
"Teddy-Z"
"NFX"
"That NF_2 Compound"
"That HMX Analogue"

First Synthesis of TEDDZ

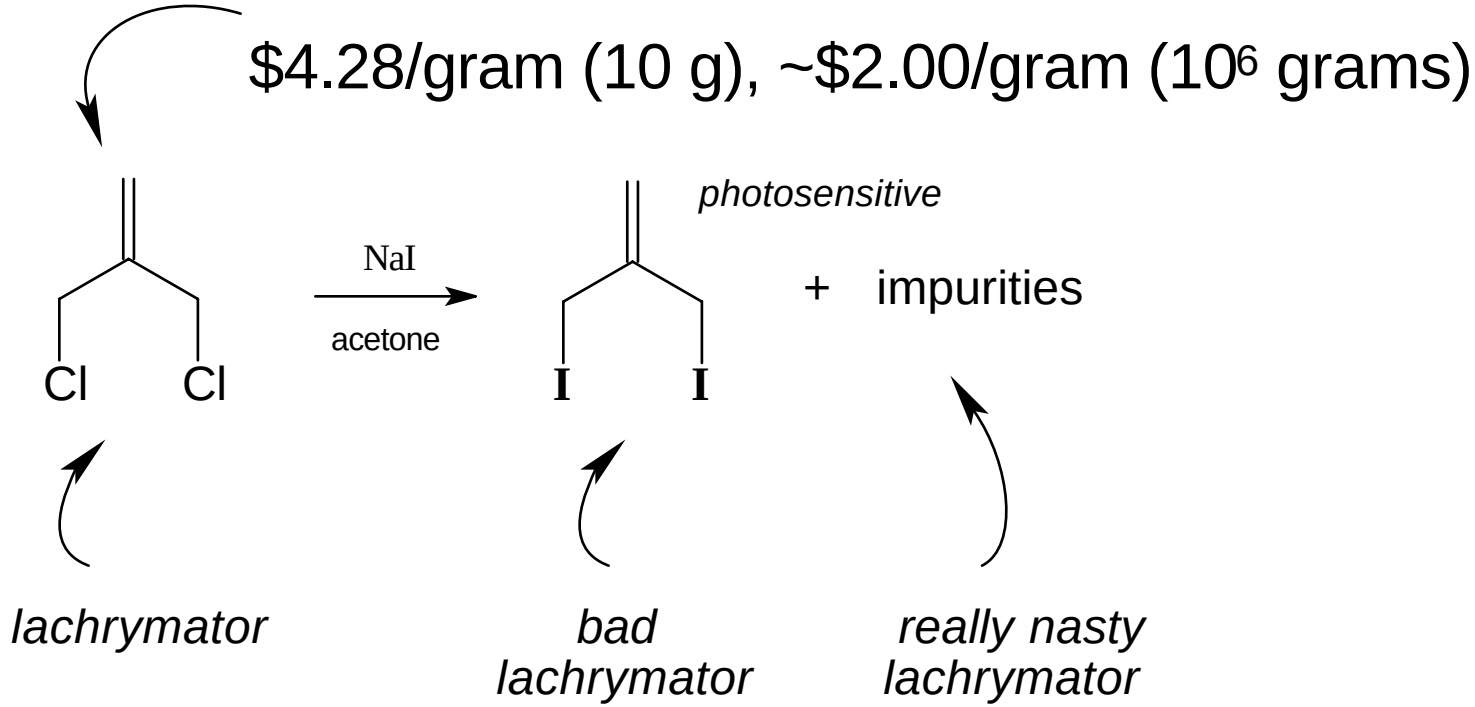


(Chapman, Fluorochem)

Original Route Drawbacks

- Starting material
- Acetyl protecting group protonated under difluoramination conditions ($\rightarrow$ deactivation) and unstable during prolonged reaction
- Nitramine "protecting group" unstable under difluoramination conditions $\rightarrow$ terrible yield
- Difluoramine (HNF_2) treacherous

Methallyl Dihalide Route



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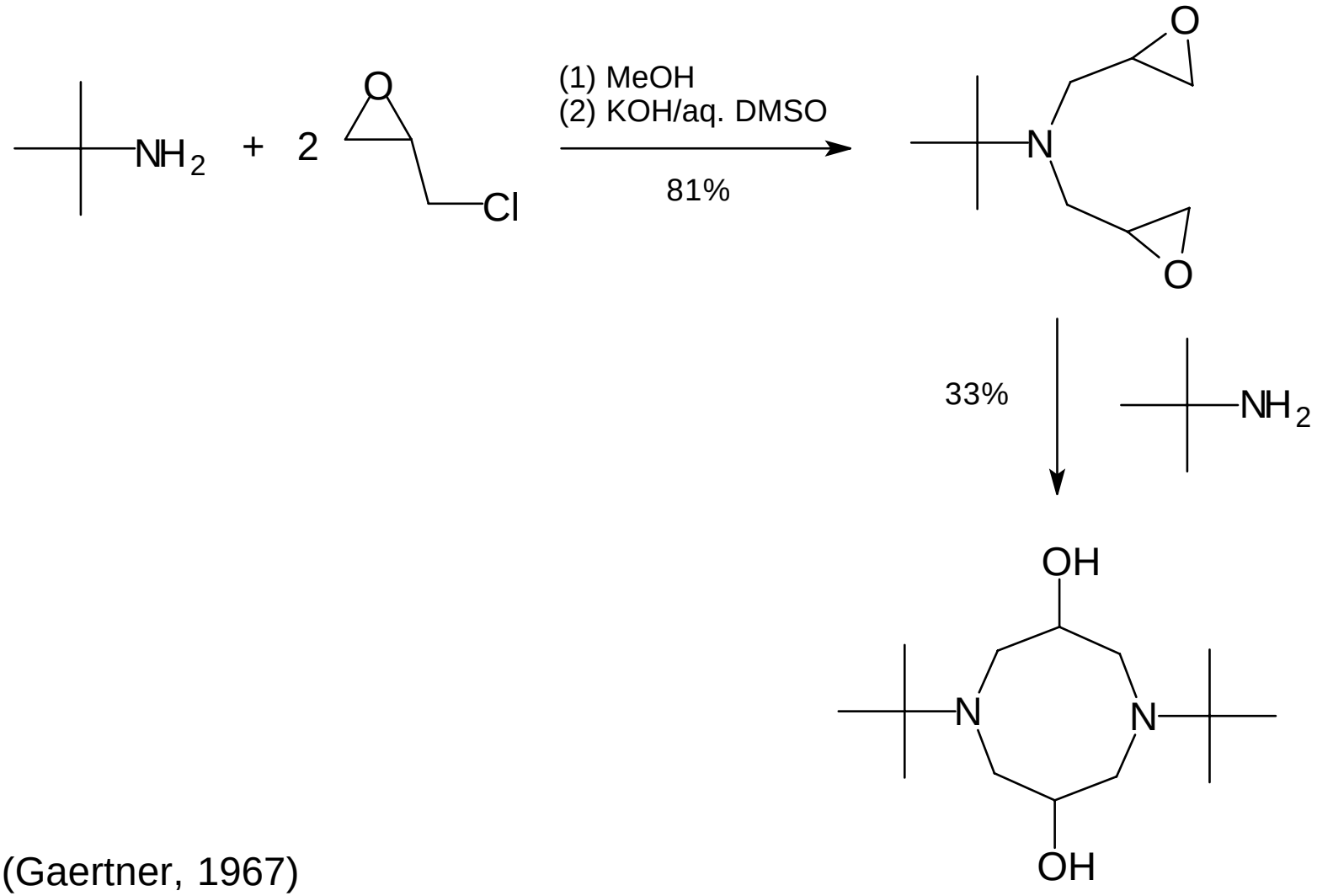
Alternative Diazocine Preparations



(Gaertner, 1967)

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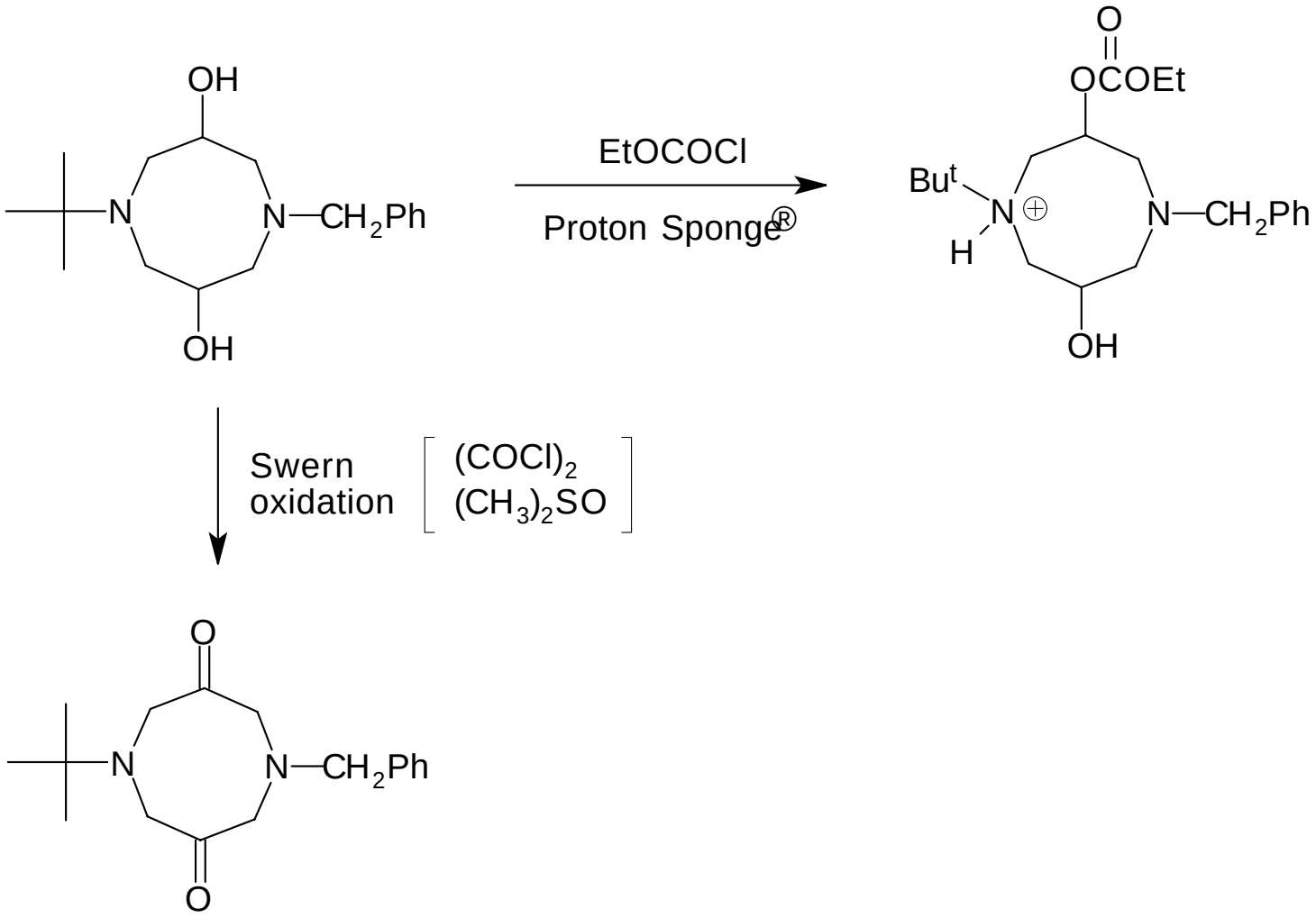
New Diazocine Derivatives



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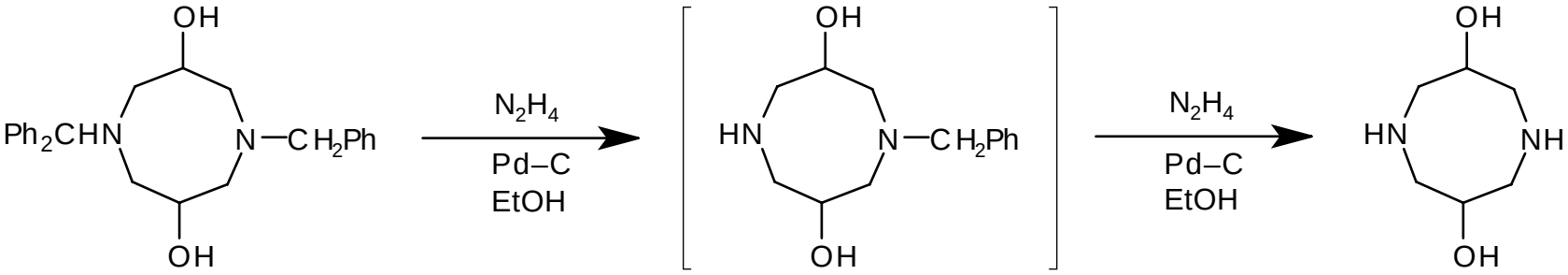
New Diazocine Derivatives

- *N*-Benzyl and *N*-benzhydryl easier to dealkylate than *t*-butyl



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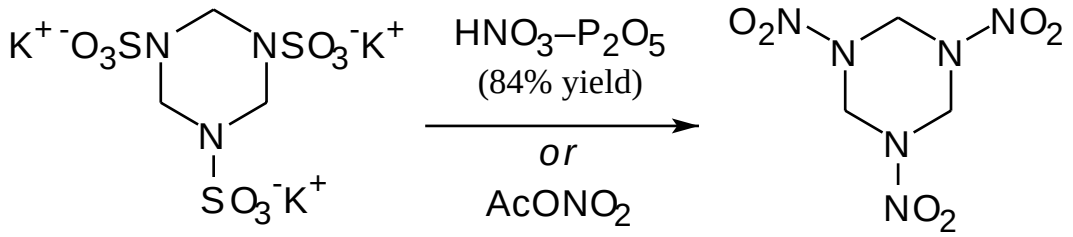
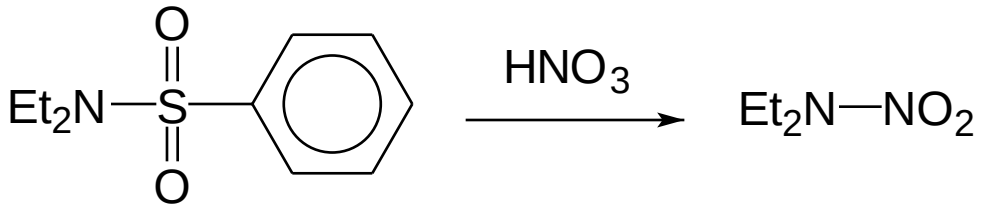
Acid-Stable Nitrogen-Protecting Groups

- Sulfonic acid derivatives amenable to nitrolysis



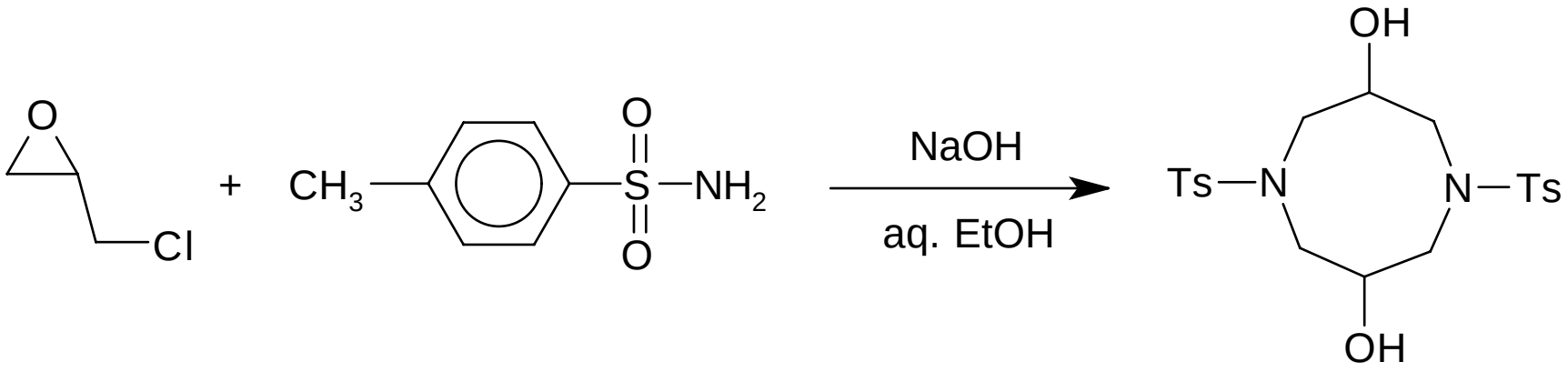
(Wright, 1950)



(van Romburgh, 1884)

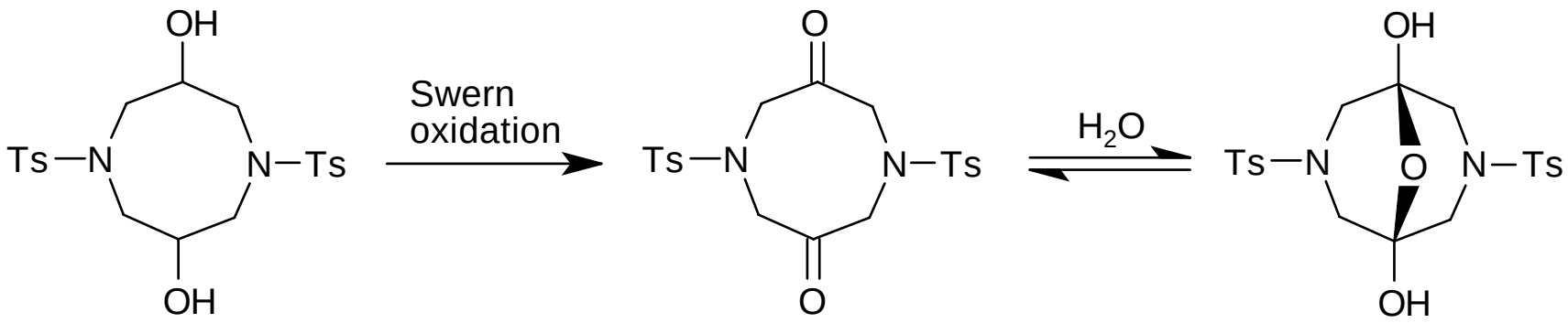
- Sulfamic/sulfonic derivatives stable to sulfonating environment

Alternative Diazocine Preparations

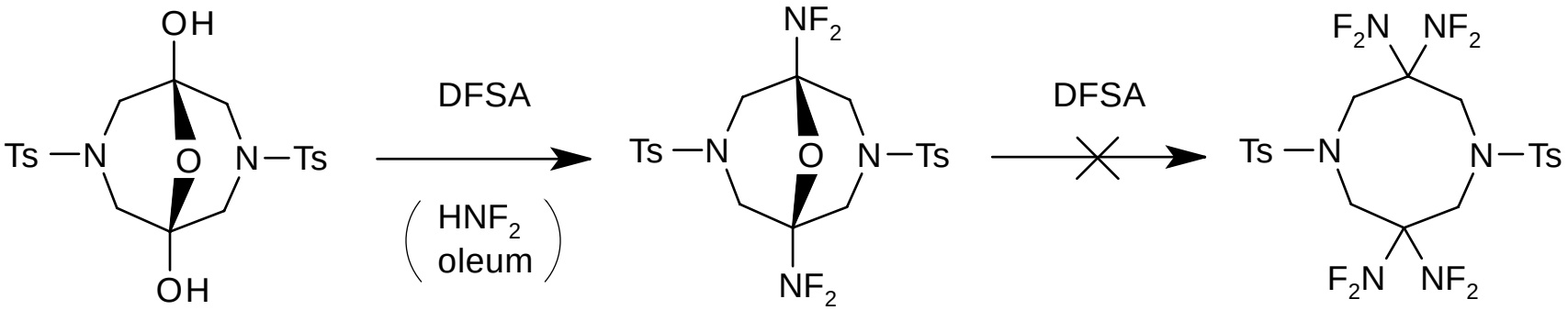


(Paudler & Zeiler, 1967)

Diazocinediones



Diazocinedione Difluoraminations



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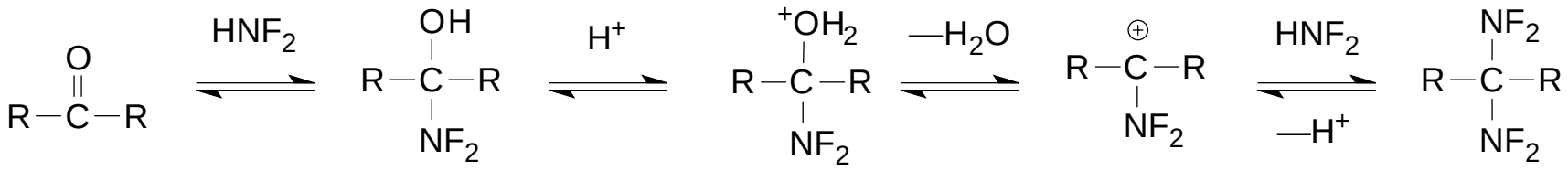
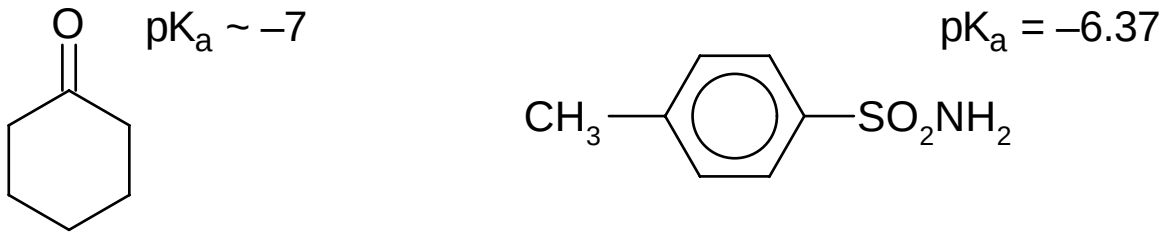
Difluoramination Mechanism

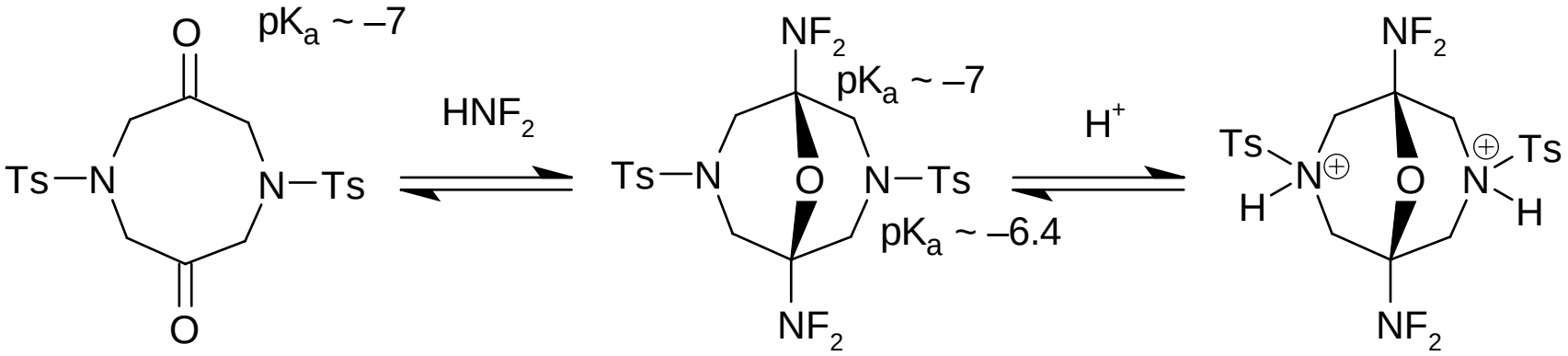


(Baum, 1968; Graham & Freeman, 1969)

Difluoramination Dilemma

- Diazocinedione basicities





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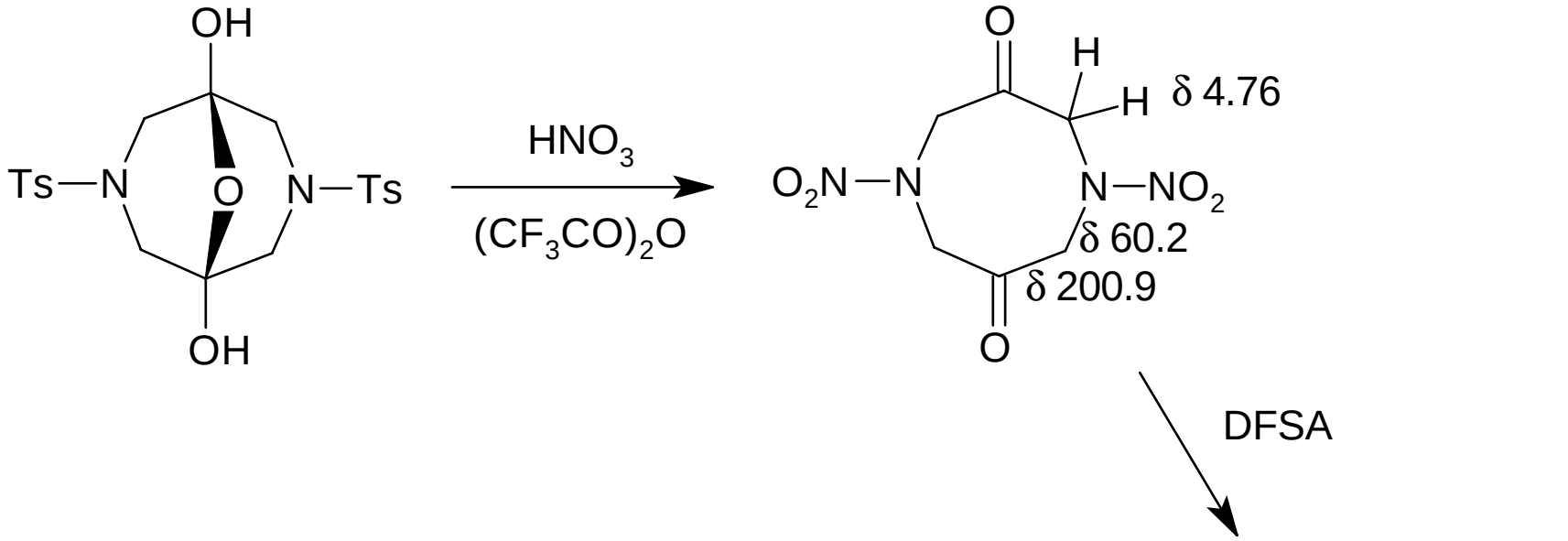
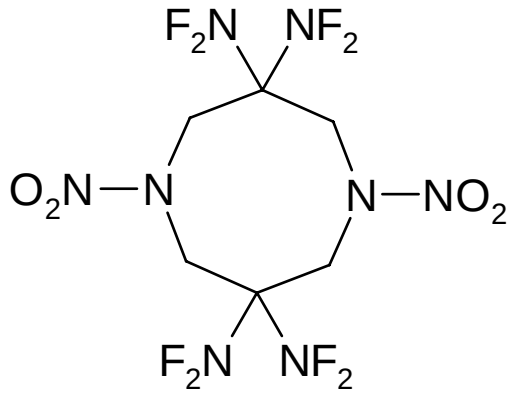
Alternative Protecting Groups



Nitramines unstable in strong non-nitrating acids
(Holstead & Lamberton, 1952;
Simecek, 1957, 1961;
Semel *et al.* 1959;
Urbanski & Zylowski, 1967)



~1% (many conditions)

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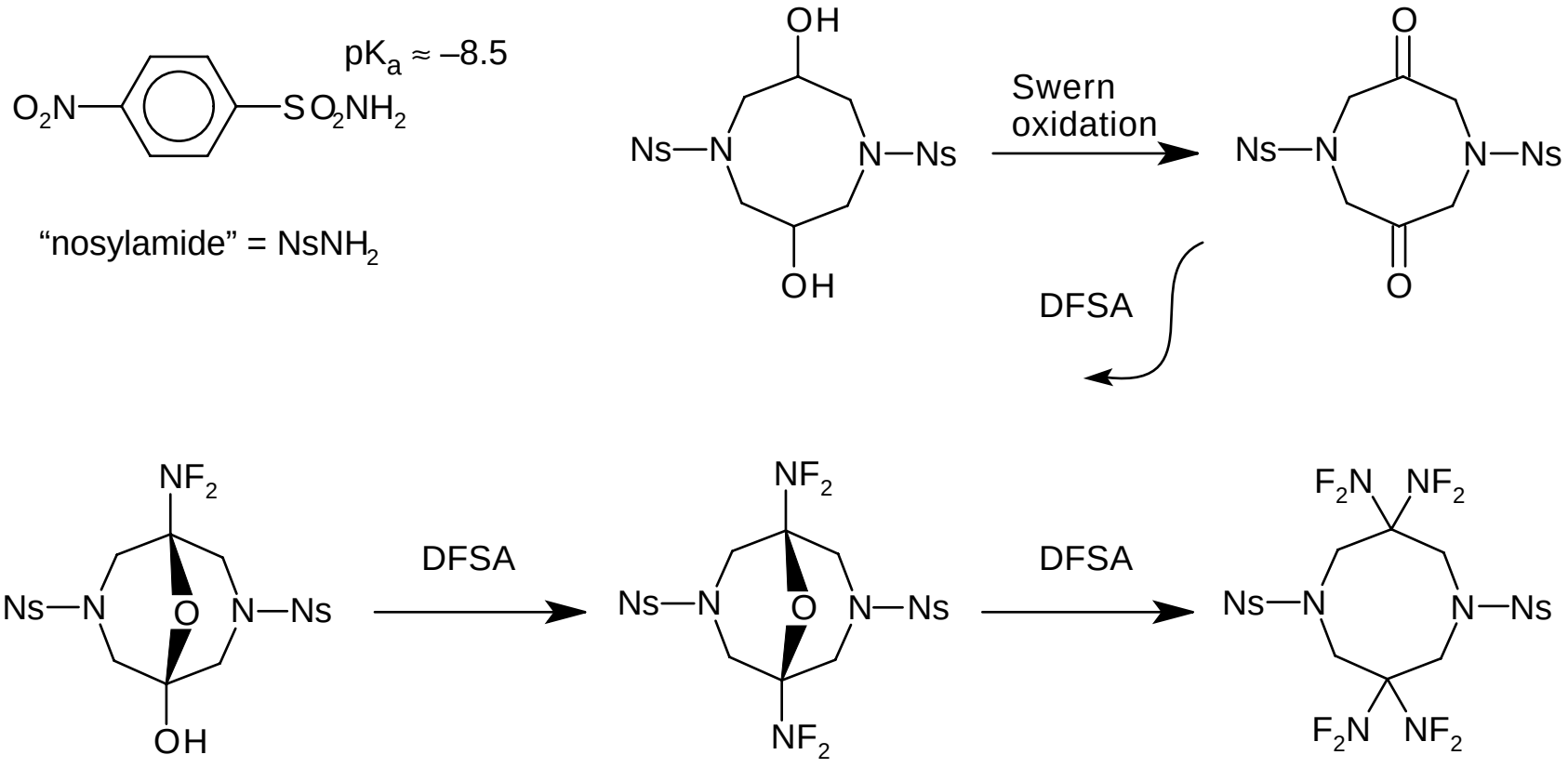
Alternative Protecting Groups



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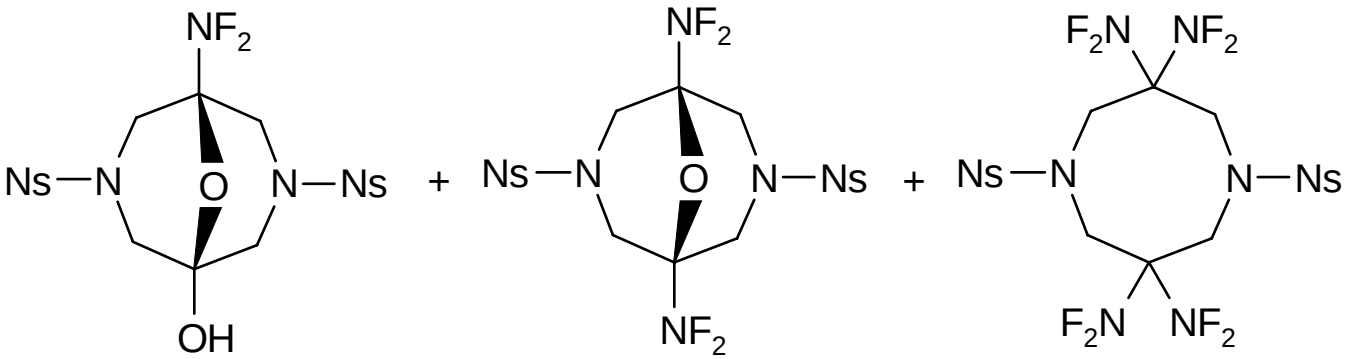
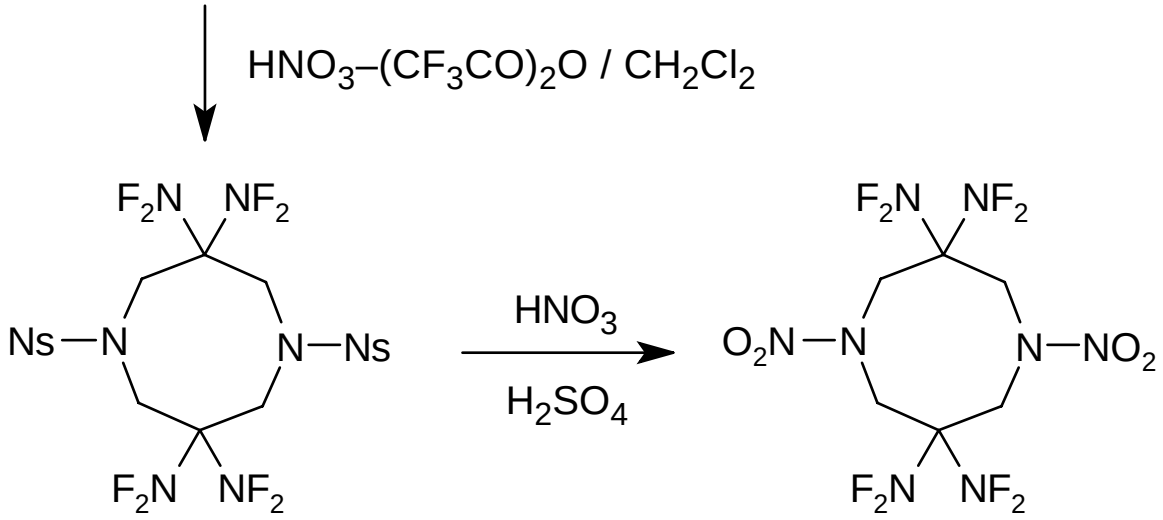
Nosyldiazocine Nitrolysis





55 °C × 12 days →
100% conversion (clean);
70 °C × 6 days →
100% nitrolysis
(incl. 14% impurities);
90 °C × 2.5 hours →
44% conversion
(+ 16% impurities)

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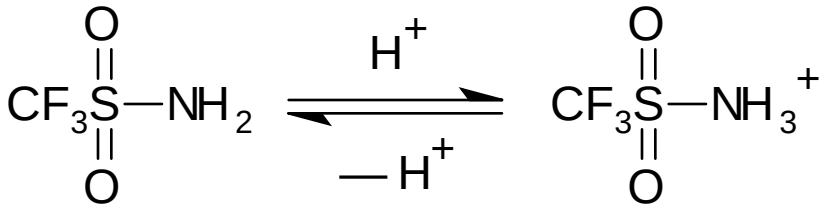
Alternative Nitrogen-Protecting Groups

- Trifluoromethanesulfonamide basicity



Solvent	H_0	^{19}F NMR (δ)		
$CDCl_3$		–79.40		
D_2O		–79.95		
D_2SO_4	–9.3	–78.99		
0.5% SO_3–H_2SO_4	–11.1	–79.71 (57%)	+	–75.86 (43%)
15% SO_3–H_2SO_4	–12.8			–75.75
15% SO_3–H_2SO_4 + 20% D_2O		–78.97		

pK_a ~ –11

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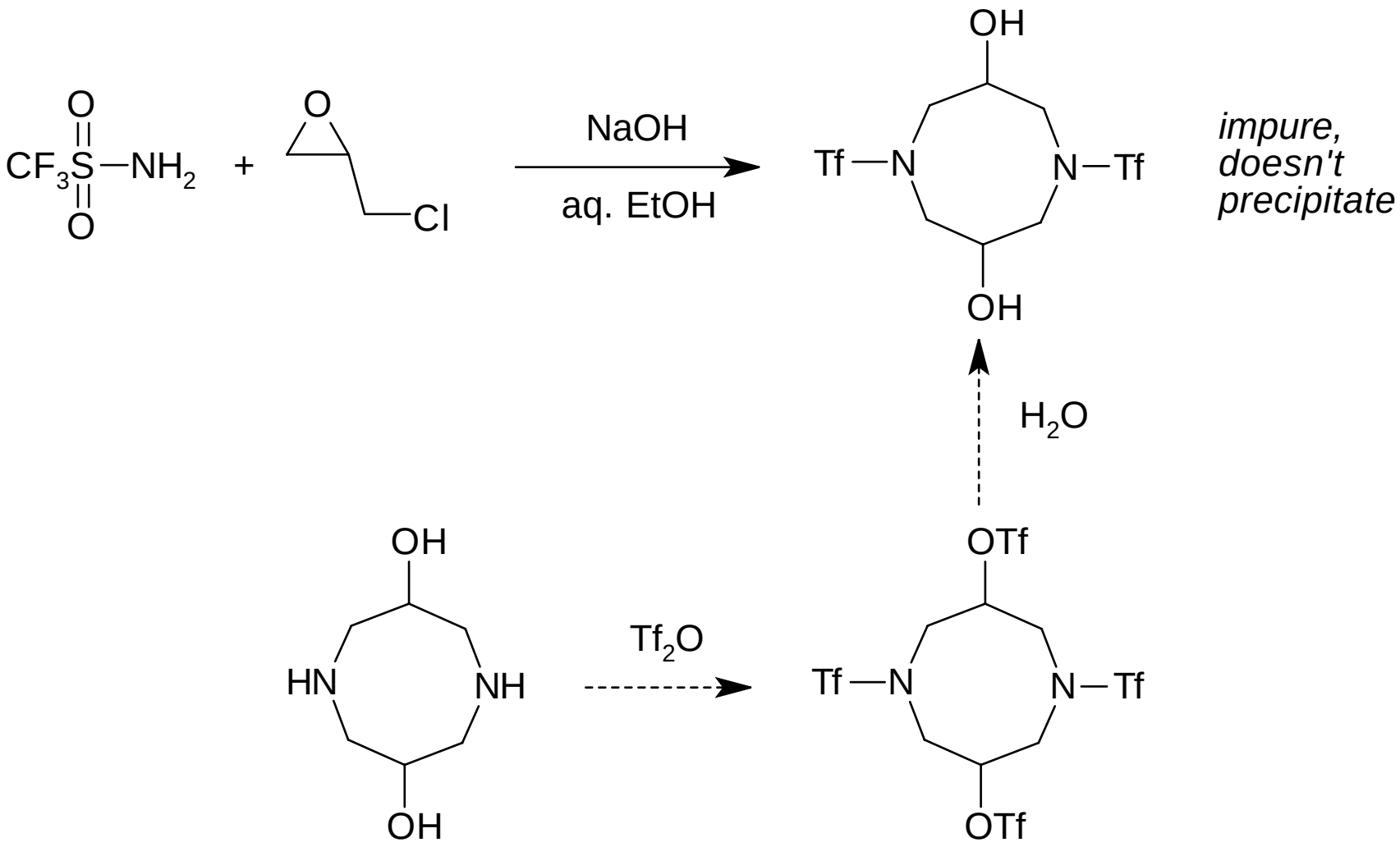
Trifyldiazocines



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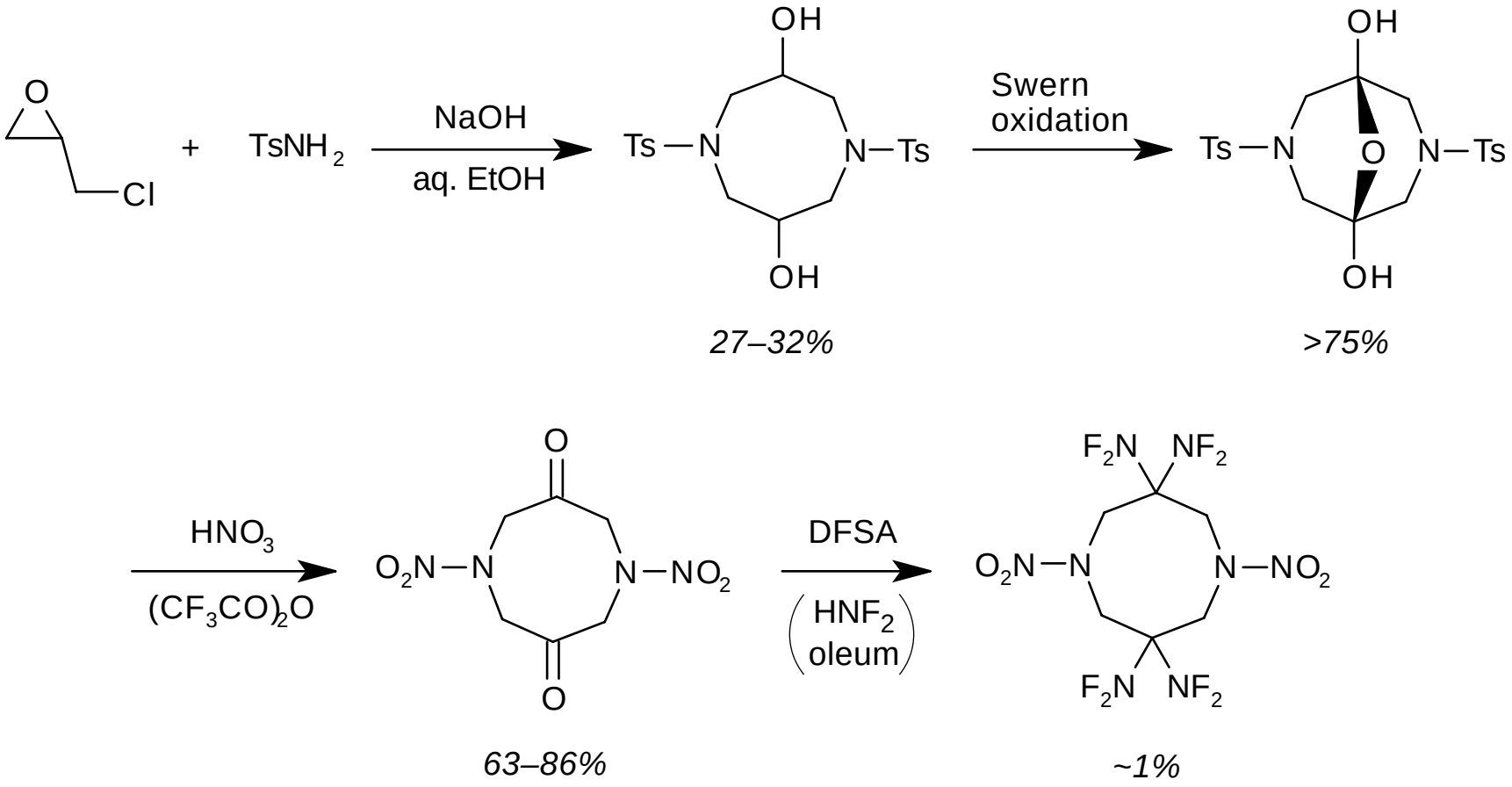
The Best Demonstrated Route to TEDDZ



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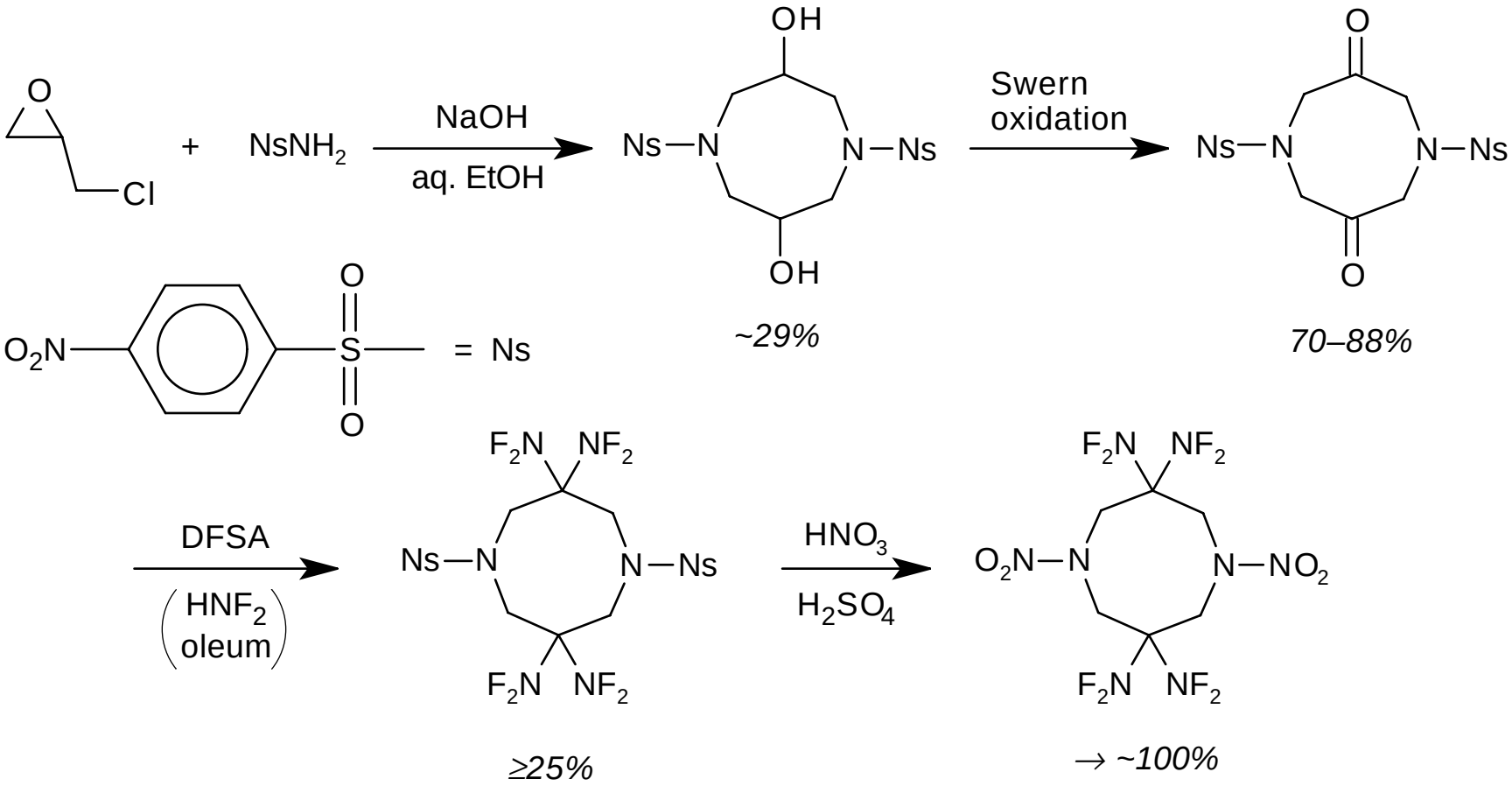
The Best Apparent Route to TEDDZ



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TEDDZ Properties

- M.P. 202~203 °C(dec)
- Readily forms solvent adducts as HMX does
- Crystal structure (solvate) by Richard Gilardi (NRL)
- TEDDZ·solvent ρ 1.784
- Comparison of solvent adduct densities:

α-HMX	ρ 1.838
HMX·DMF	1.607
HMX·NMP	1.570

Δρ ≈ 0.25

TEDDZ·solvent ρ = 1.784

⇓ Δρ ≈ 0.25

TEDDZ ρ ≈ 2.03

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Difluorosulfamic Acid (DFSA)

- NF_2SO_3H, a discrete species under typical difluoraminating conditions (Shoults/Rohm & Haas, 1967; Coon/SRI, 1973; Frankel *et al.*/Rocketdyne, 1979)

$$HNF_2 + SO_3 \rightarrow NF_2SO_3H$$

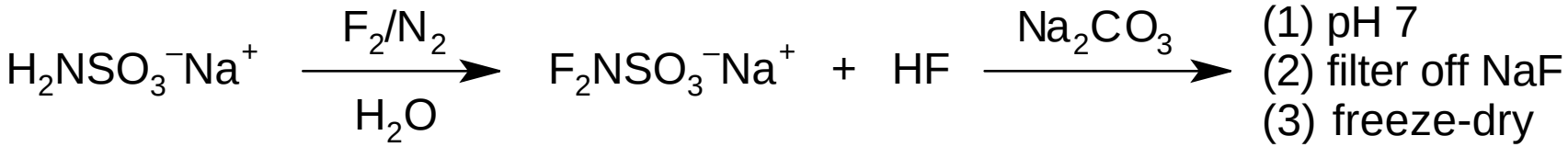
- Speculation about the nucleophilic species:

$$H_2SO_4 + NF_2SO_3H \rightleftharpoons HNF_2 + H_2S_2O_7$$

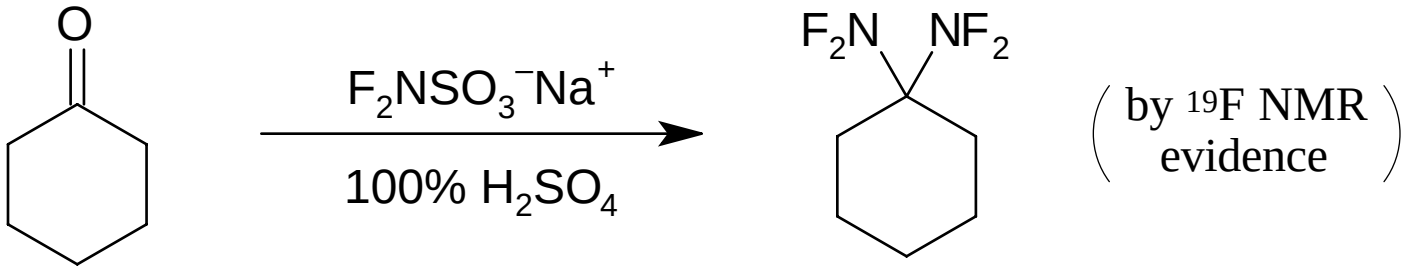
- DFSA is moderately stable in aqueous solutions (Archibald & Chapman, Fluorochem, 1990; Allied Chemical, 1961)

Alternative Difluoramination Reagent

- Sodium difluorosulfamate (Na-DFSA)



- Model difluoramination



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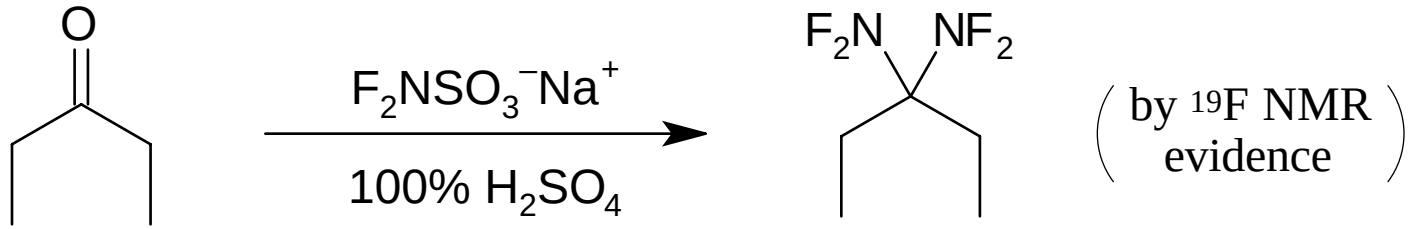
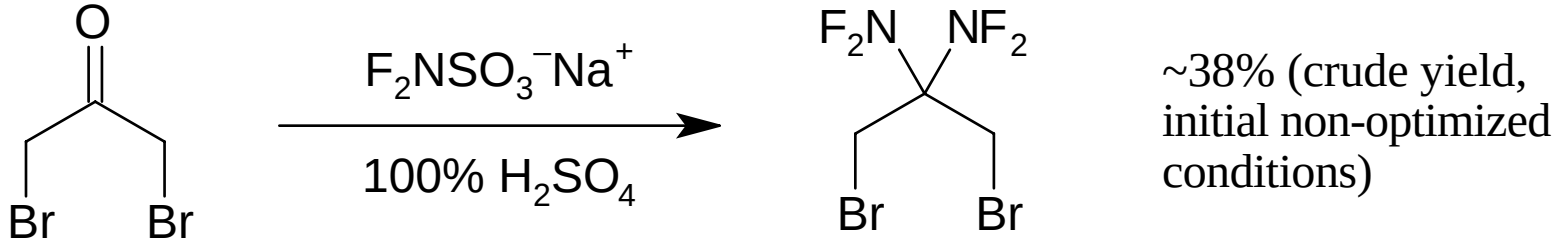
Sodium Difluorosulfamate

- Another model difluoramination



- A safe, convenient reagent of preparative utility!



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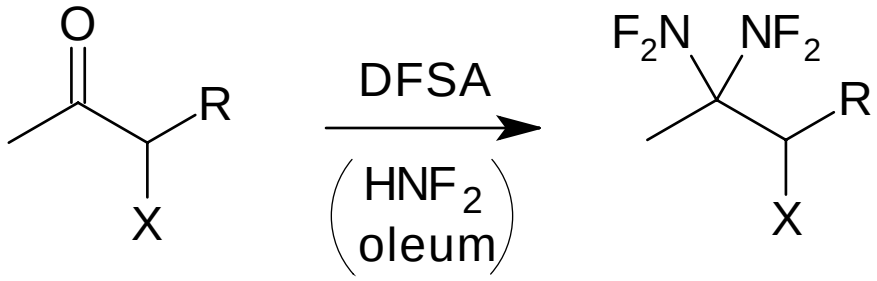
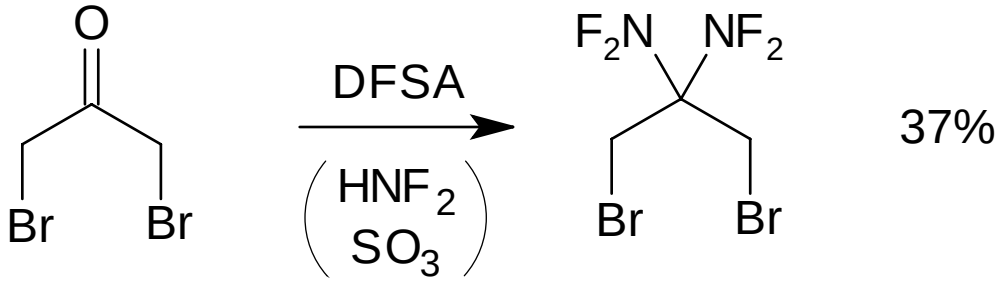
gem-Bis(difluoramino)alkyl Halides

- α-Haloketone difluoraminations



X = Cl, R = H (Mitsch, 1968; Baum, 1968)
X = Br, R = H (Fokin, 1978)
X = Br, R = CH_2Br (Orlando, 1971)



37%

(Esso Research, 1962)

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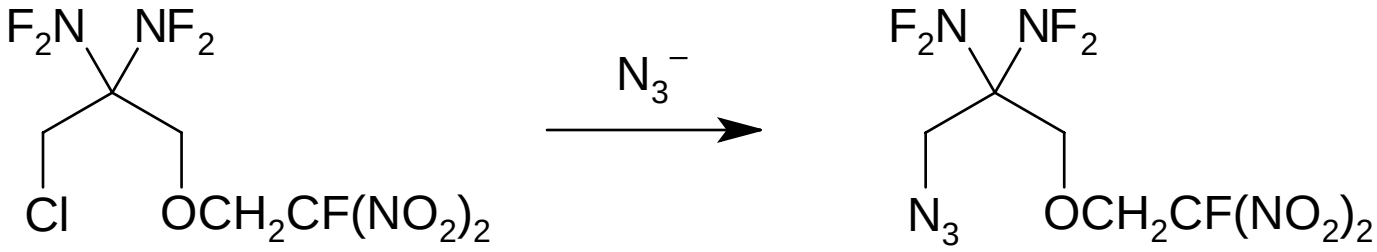
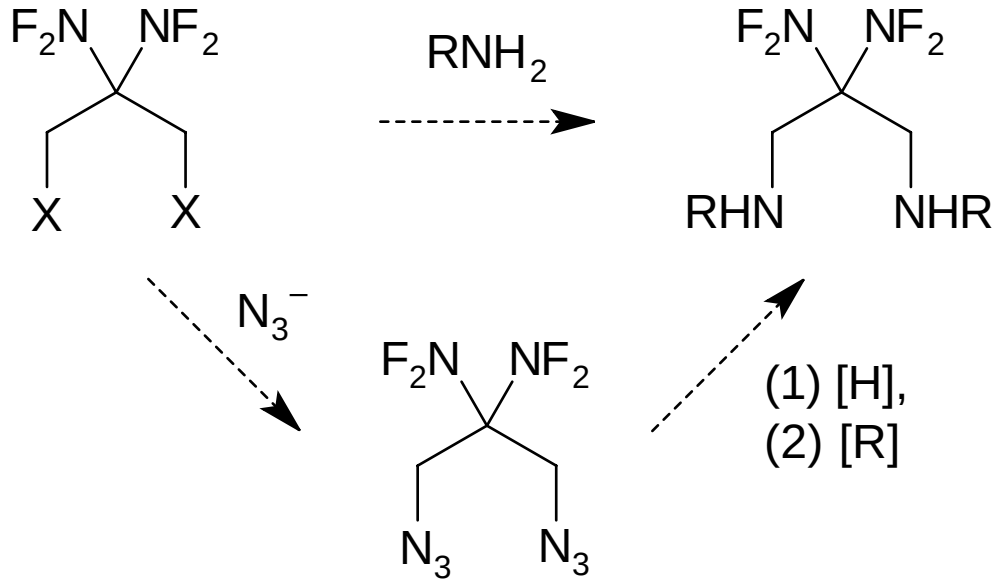
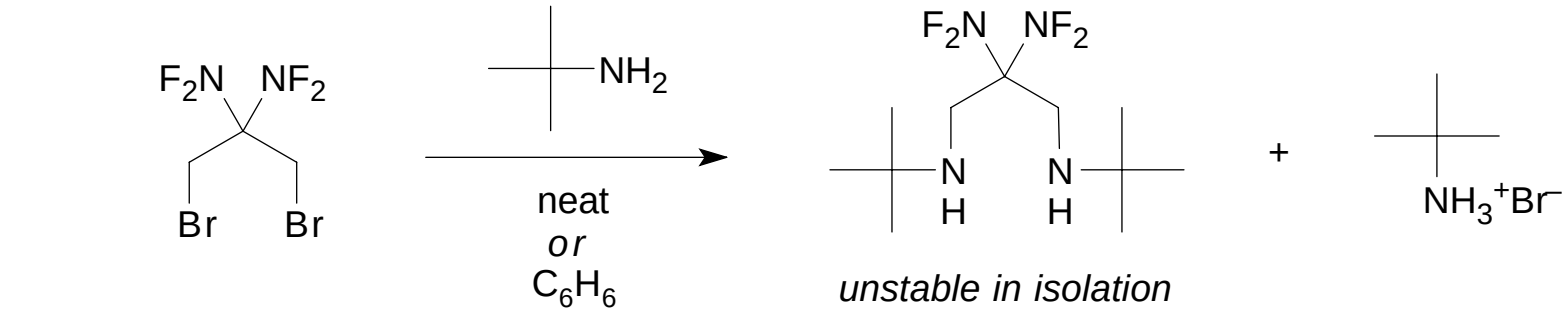
gem-Bis(difluoramino) Diamines (Retrosynthetic)

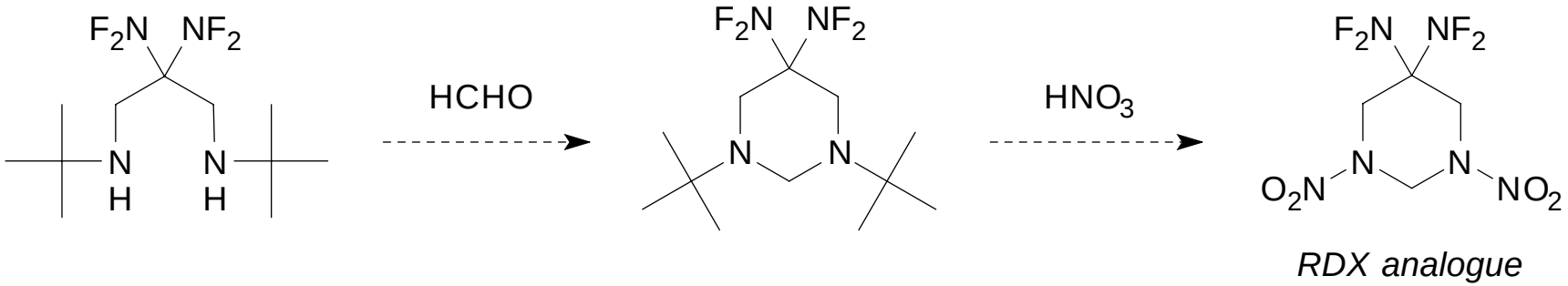


(Frankel & Witucki, 1982)



A *gem*-Bis(difluoramino) Diamine (Preliminary Result)





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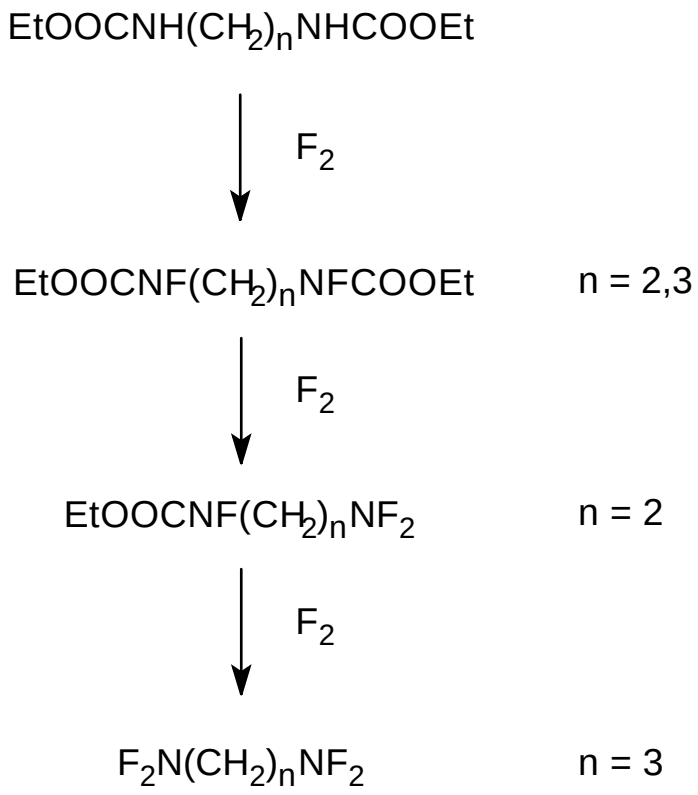
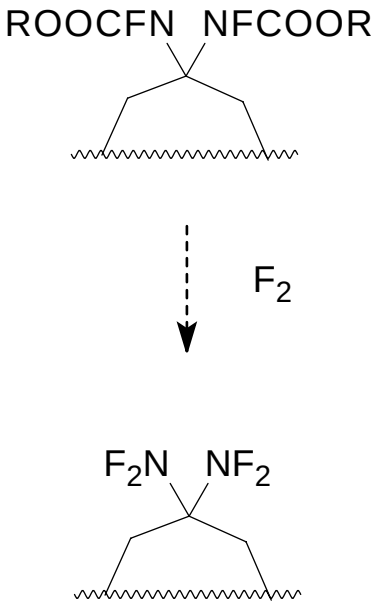
Alternative Difluoramination Methodology (Proposed)

- Fluorination of *N*-fluorocarbamates



(Grakauskas & Baum, 1969)



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Conclusions

- *gem*-Bis(difluoramino)-substituted nitrogen heterocycles pose an inherently difficult synthesis
- TEDDZ offers great prospects but experimental complications
- Diazocinedione basicity is main obstacle
- Alternative routes to this system are being pursued
- Alternative difluoramination reagents are being pursued

Acknowledgments

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